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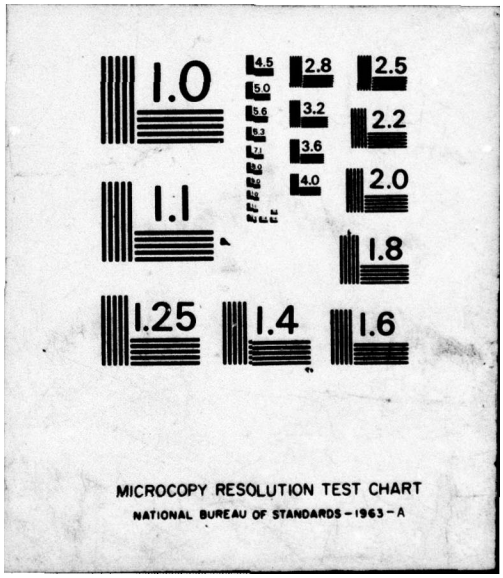
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The major advance made in the work supported under this Grant has been the development of what appears to be a very generally applicable procedure for carrying out ab initio calculations employing only the valence orbitals of atoms molecules and presumably also of solids, and using a potential function to describe the charge distribution of the cores and the Phillips-Kleinman pseudopotential technique to account for the other interactions between the fully described valence orbitals and the emulated core orbitals. [illegible] were also made in describing quantum-chemical results obtained on various molecular structures in terms which are readily interpretable to the [illegible] chemist.

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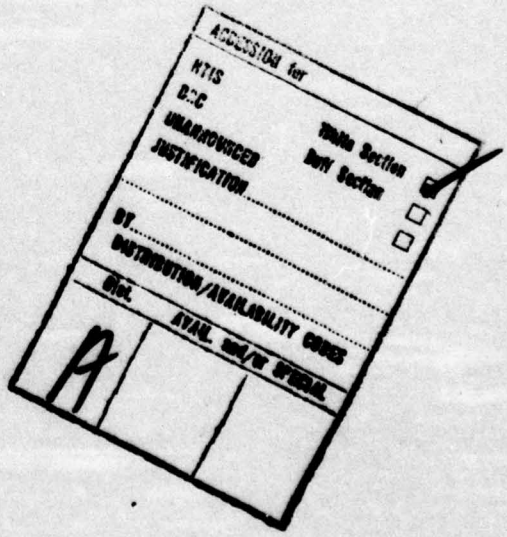
ABSTRACT

The major advance made in the work supported under this Grant has been the development of what appears to be a very generally applicable procedure for carrying out *ab initio* calculations employing only the valence orbitals of atoms, molecules and presumably also of solids, and using a potential function to describe the charge distributions of the cores and the Phillips-Kleinman pseudopotential technique to account for the other interactions between the fully described valence orbitals and the emulated core orbitals. This new method is now being subjected to further extension and development under our new continuation Grant AFOSR-77-3145. During the period of Grant AFOSR-72-2265, some advances were also made in describing quantum-chemical results obtained on various molecular structures in terms which are readily interpretable to the practicing chemist and materials scientist.



APPLIED QUANTUM CHEMISTRY OF NONMETALLIC MATERIALS

I. INTRODUCTION

The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed which can lead to an explanation of the main features of complex atomic systems without too much computation.
- P. A. M. Dirac, Proc. Roy. Soc., 123, 714 (1929).

In the Grant Proposal for AFOSR-72-2265, the proposed studies were divided into the following groups: (1) improved SCF calculations, (2) computations on various molecules, (3) development of *a priori* methods, and (4) calculation of properties. During the period of this Grant, some effort was expended on all of these areas, with emphasis on items 1 and 2. At the time this Proposal was written, it was very clear to us that a formidable major problem in applying reasonably reliable quantum mechanical calculations to all of the various elements of the Periodic Table lay in the fact that such a large proportion of the total computational effort must be devoted to optimizing the core electrons, even though the mathematical description for the core of a given atom varies only slightly from one molecular environment to another. The reason for this is that quantum calculations are usually carried out by energy optimization and

the core electrons make by far the largest contribution to the total electronic energy. For example, even in the case of a Second-Period element (such as carbon) which has only a single pair of core electrons per atom, about 75% of the cost of a full self-consistent-field (SCF) molecular calculation is due to the presence of the core. For the heavy atoms, the high cost of a full-SCF study is nearly all due to the presence of the core electrons.

In the original proposal, we suggested several ways for avoiding the core problem. These suggestions lay in two classes: one consisting of some way of modeling the core electrons; and the other, some improvement in the semi-empirical approach whereby the core is simply ignored by adjusting the nuclear charge so as to correspond to the sum of the charge of the nucleus and of the omitted core electrons.

II. A BRIEF REVIEW OF THE WORK PUBLISHED UNDER THIS GRANT

A. Ab-Initio Studies on Various Molecules, With all Core Electrons Included. The first six papers supported under this Grant dealt with *ab initio* calculations, using a moderately sized Gaussian basis set, on a collection of molecules chosen because of their special chemical interest. In our study of the PF_2H and OPF_2H molecules,[1] it was found that 9 of the 10 valence-shell molecular orbitals of PF_2H are individually closely related to 9 of the 12 valence-shell molecular orbitals of OPF_2H, with this close relationship showing up in the electronic population, electron-density plots, and orbital energies. In addition, the valence-shell molecular orbitals were correlated with those of the PF_3, OPF_3, PH_3, and OPH_3 molecules; and it was shown that some of the molecular orbitals persist practically unchanged from one molecule to another in this set of not closely related molecules. In the study of the electronic structures of phosphirane and thiirane,[2]

it was shown that the valence orbitals of the cyclic molecules, C_2H_4PH and C_2H_4S are closely related and that these are quite similar to the respective orbitals of cyclopropane. These two papers[1,2] indicate quite clearly that not only are the delocalized molecular orbitals obtained from self-consistent-field calculations about as readily understandable and interpretable in chemical terms as are the localized orbitals derived from them, but that some of the delocalized orbitals of one molecule may reappear practically unchanged in a related structure. We concluded in these studies that there are probably a relatively limited number of SCF delocalized orbitals which are to be found over and over again in common chemical compounds. It was suggested that these "molecularly invariant" orbitals should be of great importance in practical chemistry and that their contributions to properties (such as the electron-binding energy, the contribution to the electronic part of the dipole moment, etc.) ought to be intercompared to give a better insight into the electronic structure of matter.

In an *ab inito* study[3] of the role of d orbitals in chlorosilane, the electron-density plots demonstrated that conferring d character upon either silicon or chlorine has about the same effect on the detailed transfer of charge between the chlorine and silicon atoms. However, the usual population analysis leads to the conclusion that, when d character is allowed only to the silicon, there is a $p_\pi - d_\pi$ transfer of charge from the chlorine to the silicon but, when it is allowed only to the chlorine, the effect is essentially just a polarization of this atom. In other words for this example (and presumably in the usual case), there is really essentially no physical difference between $p_\pi \rightarrow d_\pi$ charge transfer from atom B to atom A and simple polarization of the charge of atom B towards A.

It was also pointed out in this work that the calculated variations in the orbital energies of the core electrons upon allowing or disallowing

d character to the silicon or chlorine atoms may be interpreted in terms of changes in the electrostatic potential in the core region. These findings have significance with respect to the interpretation of data from inner-orbital photoelectron spectroscopy.

The next two papers[4,5] deal with the role of d orbitals in a sulfur and a phosphorus compound, employing *ab initio* SCF calculations with a moderately sized Gaussian basis set. In the first of these studies,[4] the electronic structure of isothiocyanic acid was calculated and then compared with that calculated for isocyanic acid; and it was concluded that (a) the π system in HNCS involves a nitrogen lone pair stabilized by a higher-lying C-S π bond, while the π system of HNCO consists of a C-O π bond stabilized by the higher-energy nitrogen lone pair and (b) the d orbitals of sulfur are accepting density in a σ rather than a π fashion. Although we put a tremendous amount of effort in our SCF study of the electronic structures[5] of phosphorus pentafluoride and tetrafluorophosphorane, it turned out that we were scooped in our publication by Strich and Veillard.[6] Since these authors employed a larger basis set than we did, our publication[5] as it finally appeared represented a considerable condensation of our full study. Not surprisingly, our calculated results were quite similar to those of Strich and Veillard. However in our work, we emphasized the electronic structures of the individual orbitals and the correlation of the orbitals of PF_5 with those of the PF_4H, OPF_3, and PF_3 molecules.

The electronic structure of dinitrogen tetroxide and diboron tetrafluoride were determined[7] in SCF calculations involving a moderately-sized basis set. Since one of these isoelectronic molecules (N_2O_4) exhibits a planar equilibrium structure in the gas phase while the other (B_2F_4) apparently has a rather small rotational barrier, their conformational stabilities were calculated. Our analysis indicated that the conformational stabilities were determined primarily in terms of lone-pair interactions between nonadjacent oxygen or fluorine atoms,

along with lone-pair donations into the central σ^* bond. The electronic structure of these molecules was interpreted in considerable detail and it was shown that previously suggested[9] electronic configurations for nitrogen tetroxide (in which the NO_2 units are bonded only by π interactions) are dissociative and hence of little importance. Our conclusions were in agreement with the available spectroscopic data on this molecule.

Some of these ideas were developed in a book entitled "Electron Density in Molecules and Molecular Orbitals" which was published from our laboratory in 1975, with the proceeds being freely donated to Vanderbilt University. In this book, we have pointed out how electron-density plots may be used to explain and interpret quantum-mechanical results. Two of the more important features of this book are (a) the idea of "molecularly invariant" molecular orbitals, as described in a preceding paragraph and (b) the effect of internal rotation on electron-density distributions of the various valence orbitals in a molecule.

B. Calculations with the Core Electrons Omitted. A great deal of effort was spent in this area and much of it was not published, since we were unhappy with the results and saw no reason to clutter up the literature with it. Many of the original ideas (such as the lumped core) suggested in the Grant Application simply did not work out in the long run, although for a while they looked promising enough for us to sink considerable effort into them. Much the same thing could be said about our attempts to improve the various semi-empirical techniques so as to make them less empirical and more generally applicable. Of this kind of work, only one investigation was published.[10] This paper presents a description of the new DVMO (directed-valence molecular orbital) method; which is based on the idea that, for the results of an approximate MO method to be invariant upon rotation of the molecular coordinate

system, there is no requirement that directed-valence effects (e.g. the difference between σ and π p-type orbitals) be neglected in the one-center Fock-matrix elements. This new method, in which these effects are accounted for, was applied to a group of diatomics and found to give reasonably good results. However, even though this was the best of our endeavors along this line, we do not particularly recommend our new method for general use or further development since it doesn't lead to significant improvement.

When Dr. Patrick Coffey joined our group in May of 1974, we were feeling very desperate about what route to follow in order imitate or obviate the core electrons of a SCF calculation. We had considered the pseudopotential and effective-potential techniques, but only in passing because the available literature seemed to indicate that this approach did not afford an appropriate basis for the development of a generally applicable practical method for carrying out LCAO-MO-SCF calculations. However as a last desperate gamble, Dr. Coffey looked into this method to see if it could be developed in such a way that it would be suitable for routine quantum-chemical studies. Fortunately, he found a way to do this, an approach which has been described in the first paper from our laboratory dealing with our new NOCOR (Neglect of Core ORbitals) method. In this first paper,[11] the method was applied to the main-group atoms, ranging from atomic number 2 through 36, as well as to the molecules C_2, Si_2, Ge_2, and PF_3. The findings on these atoms and molecules were compared to conventional SCF results in comparable basis sets and to experiment for the C_2 and PF_3 molecules. We were particularly pleased that our electron-density plots of the valence orbitals of the diatomic molecules (C_2, Si_2, and Ge_2) showed that the spacial distributions outside of the core region appeared to be very similar to those obtained from the equivalent full-SCF calculations.

The next paper[12] on the NOCOR method dealt with the application of this approach to the four PX_3 phosphorus halides (X = F, Cl, Br, and I), with the geometries being optimized and the force constants, orbital energies, Mulliken populations and dipole moments being calculated using a minimum-Slater valence basis set.

These first two papers represented a practical test of our ideas of how pseudopotential theory might be applied to everyday quantum-chemical calculations; and these two publications showed that the approach was worthy of further consideration. A problem that often comes up in theoretical work is the question of how much effort should be put into theoretical developments before the underlying ideas have been tested as to their usefulness and practicability. In our laboratory, we usually take the general approach of first testing the usefulness of a theoretical advance while the theory is still in a state of flux and is far from being worked out well. If the preliminary practical tests show merit, we then attempt to investigate the theoretical details.

Our first careful theoretical investigation of the new computational procedure (the NOCOR method) was described in a paper[13] which appeared in 1975. In this, the theory of pseudopotentials and effective potentials was investigated and properly extended to cover the approach we had developed. This theoretical study indicates the following: (a) increasing the size of the basis set requires a concomitant increase in the complexity of the model potential used to describe the core. A minimum-Slater basis set works well in these calculations because the atomic and molecular eigenfunctions are "locked" into essentially the same shape. However, the use of a more flexible basis set (such as a double-zeta set), requires a more accurately defined shape of the model potential in the valence region, and in this study we found that

at least two mathematical terms (instead of a single one for the single-zeta case) were required for this purpose. (b) We did not find any evidence for failure of the frozen-core approximation, whereby the core model-potential of an atom (in the form of an atom or ion, or present in a molecule) is considered to be unchanged by the differing environment due to the various distributions of the valence electrons in the different systems. This conclusion indicates that there is no need for core-polarization potentials, as has been suggested by others. Furthermore, (c) this work has indicated that the NOCOR procedure is about as accurate as the corresponding conventional SCF calculation in determining molecular structures, vibrational spectra, dipole moments, Mulliken populations, and the influence of d orbitals.

In the next theoretical paper,[14] which is still in press, a new expression for the Phillips-Kleinman pseudopotential is proposed for many-valence-electron molecules. According to this approach, each valence molecular orbital is treated in terms of its orthogonality constraints with respect to the core orbitals. This is in contrast to our previous approach and those of all others, in which an approximate average pseudopotential based on the valence atomic orbitals of the free atoms is employed. Our new formulation of the problem results in an appreciable increase in precision, particularly for the valence-orbital energies. In addition, we derived general expressions for the local terms in the effective potential, which are not restricted to any special analytical form. We have now shown that, if the core is described precisely in terms of this local potential function representing only the Coulombic and exchange interactions and if the correct Phillips-Kleinman pseudopotential is derived from our new formulation, the entire effective potential is well accounted for. In view of this work, we now believe that the general approach represented by the NOCOR method has been demonstrated to be fundamentally

sound and ought to be generally applicable for virtually all kinds of SCF calculations. In this paper, the new approach has been tested on the I_2 molecule; and the results obtained with it are compared with our previous approaches and with the results from an equivalent full SCF calculation. The manuscript of this important paper is presented as Appendix I in this Final Report. It now seems quite clear on the basis of this paper that the proposals for further quantum-chemical work outlined in the Grant Application for AFOSR-77-3145 (under which we are now operating) are well founded and should be suitable for practical development.

In a series of three papers[15-18] which appeared in 1976, we have applied the NOCOR method to practical problems of calculating molecular wavefunctions. In one of these investigations,[15] a calculation was carried out on the P_4 and P_2 molecules and their interconversion. In this work, the molecular geometry was optimized and the resulting bond lengths were found to be close to those measured experimentally. Upon allowing d functions, it was found that the electronic hybridization of each phosphorus atom in the P_4 molecule changes from $s^{1.90}p^{3.10}$ to $S^{1.77}p^{3.08}d^{0.15}$ resulting in considerable polymerization of the valence-electronic distribution, with the total electronic charge shifting away from the atoms towards the center of the P_4 tetrahedron and also in the P-P axial regions. Unfortunately, due to an inappropriate setting of the lower limit for calculating integrals, a mistake was made in the molecular-orbital correlation chart relating the P_4 molecule to the pair of P_2 molecules resulting from pulling a P_4 molecule apart along its C_2 axis. This error has been corrected in an erratum.[16]

The next paper[17] in this group deals with NOCOR calculations on the tetracarbonyls of nickel, palladium and platinum. We felt that it was very important to carry out soon a study on transition-metal compounds,

since some persons in this field think that any pseudopotential method simply cannot achieve reasonable results when applied to the compounds of the transition metals. In this work, we have compared the full-SCF results on tetracarbonylnickel with the NOCOR calculations on this molecule and found good agreement. However, we found that the outermost orbitals of the palladium and platinum carbonyls were in reversed order with respect to those found for the nickel compound and we spent considerable space in the paper arguing how this might have come about. However, a French scientist has now carried out a full-SCF calculation[18] for tetracarbonylpalladium and has shown that the ordering of the molecular orbitals with respect to energy in this compound is the same as in its nickel analog! This scientist has therefore entitled his manuscript "Failure of a Pseudopotential Calculation for $Pd(CO)_4$" in reference to our work. It turns out that, during the time we were engaged in this calculation, a minor error was made in the mathematical description of the core d orbitals, which are found in the core palladium and platinum, but not nickel. Therefore the nickel calculations turned out correctly but there were some minor mistakes which were big enough to change the ordering of the two outermost valence orbitals in the calculations on the palladium and platinum analogs. We are presently in the process of repeating these calculations and have already found for palladium that, when the core d orbitals are represented by correct mathematical expressions, the so-called "failure" of the pseudopotential method disappears. We are happy that the error was a human one and is not an inherent disadvantage of the NOCOR method.

The third paper[19] of this group deals with the use of the pseudopotential method in calculating barriers to internal rotation. In this work, the barrier to internal rotation as computed by the NOCOR method for ethane, methylsilane, methylgermane, and methylstannane, were compared with conventional SCF results for all but CH_3SnH_3 and in each case with experiment.

As expected, the NOCOR results turned out well. Analysis of the NOCOR barrier (based solely on the valence orbitals) indicates that the pseudopotential formulation (which is included in the one-electron part of the Fock matrix) effectively incorporates the entire core/valence interaction, including the omitted two-electron contributions. Therefore, the pseudopotential method has now been shown to work for calculating internal-rotational barriers; and this occurs because of the relative invariance of the omitted core and core-core electronic contributions to the internal-rotation process.

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THE STRUCTURE OF MOLECULAR EFFECTIVE POTENTIALS IN COMPOUNDS OF HEAVY ELEMENTS, WITH APPLICATION TO I_2

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A new expression of the Phillips-Kleinman pseudopotential for many-valence-electron molecules is proposed. All remaining terms in the valence Hamiltonian, represented by a local potential, are evaluated from *ab initio* expressions based on the form of the atomic Fock operator. Sample calculations are reported for the orbital energies, equilibrium bond length and vibrational frequency of the ground state of the I_2 molecule.

I. Introduction

The concept of effective potentials and pseudopotentials for studying atomic and molecular valence-only electronic structure has in recent years been shown to be valid for an extremely wide variety of different properties and systems. In a previous paper[1] we showed that in particular the one-electron form of the Phillips-Kleinman pseudopotential[2,3] may be rigorously applied to self-consistent-field calculations of the valence electronic structure of many-valence-electron atoms and molecules. The primary advantages of this approach are that (1) the exact core-valence orthogonality of each molecular orbital may be represented by the pseudopotential, rather than being implicitly maintained at a value representing the ground-state neutral atom, as some other valence-electron approaches require,[4,5,6] and (2) the remaining terms in the effective Hamiltonian are greatly simplified, being well described by functions

which are monotonically decreasing in the valence region and very nearly the same for all symmetries of valence orbitals. That this latter condition is not generally true of other techniques has been clearly shown by the work of Kahn and Goddard,[3] *inter alia*.

The purpose of the present paper is to resolve some ambiguities in our previous formulation of the Phillips-Kleinman expression for molecules. Second, we will suggest some more rigorous and accurate expressions for the local "model" potential representing the core-valence Coulomb and exchange operators. This potential, together with the pseudopotential, we will refer to as t "effective potential". The description of the local potential is of particular concern due to the observation[1] that simple analytical expressions for the model potential seem to be inappropriate for use with double-zeta and larger valence basis sets. Some representative valence-electron results for the orbital energies, equilibrium bond length and vibrational frequency of I_2 in a minimal basis set are reported and compared to the results of an equivalent all-electron SCF calculation.

II. The Molecular Phillips-Kleinman Expression

The requirement that a molecular orbital be normalized and orthogonal to some set of functions, usually designated as the core orbitals, may be shown[1,3,6] to be energetically equivalent to relaxing the orthogonality constraint, but adding to the Hamiltonian a generalized pseudopotential term, V^{GPP}. Defining first the molecular projection operator

$$\hat{P} = \sum_{k}^{\text{nuclei}} \sum_{i}^{\text{orbitals}} |\phi_{ck}^{i}\rangle\langle\phi_{ck}^{i}| \qquad (1)$$

where ϕ_{ck}^{i} is the i^{th} core function on nucleus k, the one-electron form of V^{GPP} for Hartree-Fock calculations on systems with one valence orbital[1] is then

$$V^{GPP} = -\hat{F}\hat{P} - \hat{P}\hat{F} + \hat{P}\hat{F}\hat{P} + \varepsilon_v \hat{P} \tag{2}$$

where F is the appropriate Fock operator and ε_v is the eigenvalue of F corresponding to the valence orbital. Further, since it is assumed that the ϕ^i_{ck} are chosen to approximate the true core solutions of F, so that $F\phi^i_{ck} = \varepsilon^i_{ck}\phi^i_{ck}$, Eq. (2) reduces to the more familiar one-electron form

$$V^{PP} \equiv \sum_k^{\text{nuclei}} \sum_i^{\text{orbitals}} |\phi^i_{ck}\rangle(\varepsilon_v - \varepsilon^i_{ck})\langle\phi^i_{ck}|. \tag{3}$$

If a valence wavefunction ϕ^i_v satisfies the secular equation

$$F\phi^i_v = \varepsilon_v \phi^i_v \tag{4}$$

then Eq. (4) may be written in the equivalent form

$$(F + V^{PP})\chi^i_v = \varepsilon_v \chi^i_v. \tag{5}$$

Here χ^i_v, the pseudowavefunction, may have a much simpler functional form than ϕ^i_v. This follows from the fact that the presence of V^{GPP} or V^{PP} in the secular equation causes all the ϕ^i_{ck} to be degenerate with χ^i_v, so that χ^i_v is arbitrary in the core region within a linear combination of the ϕ^i_{ck}. Hence it may be chosen to be of a convenient form such as a single Slater orbital, or otherwise shaped in the core region. Here we will simply take χ^i_v to be the outermost Slater function used to describe the atomic ϕ^i_v on each nucleus. This provides a computationally convenient definition of χ^i_v in the core region, and resolves the ambiguity with respect to the contributions of the ϕ^i_{ck}. With this type of constraint, χ^i_v will not be identical to the exact valence wavefunction, but the valence energy will

still converge properly. Thus computation of the complex nodal structure of ϕ_v^i in the core region, required by conventional atomic and molecular SCF calculations, may be obviated.

For free atoms and molecules with only one valence orbital (or one of each symmetry), the above procedure is straightforward. However in other molecules it becomes ambiguous, since there is then a different ε_v^i for each χ_v^i. Other authors, using expressions analogous to (5) have used an arbitrary "mean" value[7] of ε_v, or implicitly kept it constant at its value in the free atom.[4-6] In our previous work, we have set ε_v equal to the lowest of the molecular orbital energies, $\varepsilon_v^{(1)}$, found iteratively.

Ideally V^{PP} should be formulated such that Eq. (5) is satisfied exactly for each χ_v^i. This may be done formally, using the fact that the χ_v^i are normalized and orthogonal, by writing the molecular pseudopotential as

$$\mathcal{V}^{PP} = \sum_{i}^{\text{valence}} \sum_{j}^{\text{core}} \sum_{k}^{\text{nuclei}} |\phi_{ck}^j\rangle(\varepsilon_v^i - \varepsilon_{ck}^j)\langle\phi_{ck}^j| \left(1 - \sum_{\ell \neq i}^{\text{valence}} |\chi_v^\ell\rangle\langle\chi_v^\ell|\right), \quad (6)$$

where ε_v^i is the i^{th} valence eigenvalue of F. $\mathcal{V}^{PP}$ designates this more general form of the pseudopotential, which is a function of the complete set of valence-orbital energies. In the iterative solution of the self-consistent-field equations, the quantities ε_v^i and χ_v^ℓ may be conveniently chosen as the eigenvalues and eigenfunctions, respectively, of the preceeding iteration. At convergence, Eq. (5) is then satisfied for <u>each</u> valence molecular orbital, ε_v^i.

It should be noted that the operator defined by Eq. (6) is nonhermitian, a condition which presents some difficulties in its direct implementation. However inspection of this form of $\mathcal{V}^{PP}$ shows that in the molecular-orbital basis it

contains off-diagonal matrix elements coupling only valence orbitals of the same symmetry type, and that these elements are generally at least two orders of magnitude smaller than the diagonal terms. Therefore for the present study we have constructed $\mathcal{V}^{PP}$ as given by Eq. (6) in the molecular-orbital basis, and then neglected the off-diagonal terms. Sample computations using this expression are given below in Section IV.

III. Construction of Atomic Model Potentials

The Fock operator in Eq. (5) depends on the coordinates of all the electrons in the system, and is hence *per se* inappropriate for valence-electron calculations. A fundamental postulate used in such calculations is the existence of at least one function W^i such that, if Eq. (5) is satisfied, then for each valence orbital of a given atom

$$(\hat{F} + V^{PP} + W^i)\chi_v^i = \varepsilon_v^i \chi_v^i \tag{7}$$

where χ_v^i is the atomic pseudowavefunction and $\hat{F}$ now depends explicitly only on the coordinates of the valence electrons. (Note that, for free atoms, $\mathcal{V}^{PP}$ may be chosen equal to V^{PP} for each atomic symmetry type.) Since Eqs. (4) and (5) represent the conditions that the total energy be an extremum with respect to arbitrary variations of ϕ_v^i and χ_v^i respectively, Eq. (7) is equivalent to requiring that the energy of the valence electrons also be an extremum with respect to variations of the χ_v^i. Thus subsequent molecular calculations using this model potential are limited to basis sets composed of functions which precisely satisfy the atomic secular equation. In a molecular calculation, W is taken to represent the superposition of the potentials of the constituent atoms. In our earlier work, we have used for each atom a single expontial function of the form

$$W^{exp}(r) = N(1-e^{-\alpha r})/r \tag{8}$$

where r is the distance from the nucleus and N is the number of core electrons. α may be determined by optimizing the ϵ_v^i values in atomic SCF calculations. We now ask what is the most general form of W^i.

One approach would be to exploit the nodeless properties of each χ_v^i to invert Eq. (7), i.e.

$$W^i = \left[(\epsilon_v^i - \hat{F} - V^{PP})\chi_v^i\right]/\chi_v^i. \tag{9}$$

Since all the quantities on the right side of Eq. (9) are known from atomic SCF results, this generates a local potential that may be subsequently employed in molecular computations. However it is easy to see that this will be successful only at the Hartree-Fock limit, since using small analytical basis sets, Eqs. (5) and (7) need not be satisfied at all points in space. In particular, they need not be satisfied in the outer or valence region of the atom, which is the most important for bond formation. Trial calculations analogous to those described below verified that, at least for minimal basis sets, Eq. (9) gives only a relatively crude molecular potential function. This and similar problems that may arise from using expressions analogous to (9) have also been discussed by Melius and Goddard.[8]

A more general condition for defining W^i is to require operator equivalence, that is

$$(\hat{F} + V^{PP} + W^i)\chi_v^i = (F + V^{PP})\chi_v^i. \tag{10a}$$

or, equivalently,

$$(\hat{F} + W^i)\chi_v^i = F\chi_v^i. \tag{10b}$$

Note that Eq. (10) is equivalent to requiring that an arbitrary variation in χ_v^i cause the same change in both the total and the valence-electron energies. However this energy change need not be zero, and hence this χ_v^i need not be the solution of an atomic secular equation.

To calculate ω^i, we first define explicitly the atomic Fock operator F for closed shells as[9]

$$F = -\tfrac{1}{2}\Delta - \frac{Z}{r} + \sum_j^{\text{closed}} (2J_j - K_j) + f \sum_j^{\text{open}} (2J_j - K_j) \tag{11}$$

where Δ is the Laplacian, Z the nuclear charge, and f is the fractional occupancy of the open shell, if any. For open shells,

$$F = -\tfrac{1}{2}\Delta - \frac{Z}{r} + \sum_j^{\text{closed}} (2J_j - K_j) + f \sum_j^{\text{open}} (2aJ_j - bK_j) \tag{12}$$

where a and b are constants for a given electronic configuration. Similarly, $\hat{F}$ for closed shells is given by

$$\hat{F} = -\tfrac{1}{2}\Delta - \frac{Z}{r} + \sum_j^{\text{closed valence}} (2\hat{J}_j - \hat{K}_j) + f \sum_j^{\text{open valence}} (2\hat{J}_j - \hat{K}_j) \tag{13}$$

and for open shells

$$\hat{F} = -\tfrac{1}{2}\Delta - \frac{Z}{r} + \sum_j^{\text{closed valence}} (2\hat{J}_j - \hat{K}_j) + f \sum_j^{\text{open valence}} (2a\hat{J}_j - b\hat{K}_j). \tag{14}$$

We also define J_v and K_v, as well as $\hat{J}_v$ and $\hat{K}_v$, to be the Coulomb and exchange operators defined over the ϕ_v^i and χ_v^i respectively, so that

$$J_v \chi_v^j = \sum_i \langle \phi_v^i | \frac{1}{r_{12}} | \phi_v^i \rangle \chi_v^j \tag{15}$$

$$K_v\chi_v^j = \sum_i \langle \phi_v^i | \frac{1}{r_{12}} | \chi_v^j \rangle \phi_v^i \tag{16}$$

$$\hat{J}_v\chi_v^j = \sum_i \langle \chi_v^i | \frac{1}{r_{12}} | \chi_v^i \rangle \chi_v^j \tag{17}$$

$$\hat{K}_v\chi_v^j = \sum_i \langle \chi_v^i | \frac{1}{r_{12}} | \chi_v^j \rangle \chi_v^i. \tag{18}$$

Further let J_v^c, J_v^o etc. be the operators over closed and open valence orbitals respectively.

Noting that the only difference between F and $\hat{F}$ lies in the two-electron operators, it is convenient to divide the W^i functionsinto two terms. The first is the total interaction between the core and valence electrons,

$$W_c^i = \left[(2J_c - K_c)\chi_v^i\right]/\chi_v^i \tag{19}$$

where J_c and K_c are defined to include all the core orbitals of the summations in (11) and (12). The second term, W_v^i, is due to valence electrons in the core region. Solving Eq. (10) for W_v^i, using Eqs. (11)-(14) we have for closed valence orbitals,

$$W_v^i = \left\{\left[2(J_v^c + fJ_v^o - \hat{J}_v^c - f\hat{J}_v^o) - K_v^c - fK_v^o + \hat{K}_v^c + f\hat{K}_v^o\right]\chi_v^i\right\}/\chi_v^i \tag{20}$$

and for open valence orbitals,

$$W_v^i = \left\{\left[2(J_v^c + afJ_v^o - \hat{J}_v^c - af\hat{J}_v^o) - K_v^c - bfK_v^o + \hat{K}_v^c + bf\hat{K}_v^o\right]\chi_v^i\right\}/\chi_v^i \tag{21}$$

assuming all the core orbitals are closed. The total potential W^i is then simply $W_c^i + W_v^i$ for a given χ_v^i.

In forming the molecular effective potential, it should be noted that

the pseudopotential defined by Eq. (6) is equally applicable to both atomic and molecular pseudowavefunctions. In a molecule such as I_2, it is useful to choose the valence atomic orbitals of the free atom to be those with the maximum principal quantum number (*i.e.* 5 for iodine), and the valence orbitals of the molecule to be those dominated by these atomic valence orbitals. The ϵ^i_{ck} and ϕ^i_{ck} of the molecule are given, to an excellent approximation, by the eigenvalues of the closed-shell Fock matrix for the free atoms in the double-Hamiltonian formalism of Roothaan.[9] As in our earlier work,[1,10] take the model potential for molecular calculations to be the superposition of the model potentials of the constituent atomic cores. Finally, the interatomic core-core interactions are represented by a reduction in each nuclear charge by N, the number of core electrons, in computing nuclear-nuclear repulsion energies.

IV. Sample Computations

To illustrate the use of the above expressions for both the pseudopotential and local model potential in determining molecular properties, we have performed both all-electron and effective potential minimal-basis-set calculations on the ground state of the I_2 molecule. This structure was chosen since it is well-known compound of reasonably heavy elements and is also amenable to full SCF calculations.

All results reported here were obtained using an atom-optimized set of Slater orbitals. Each core Slater function was expanded into three gaussian functions and each valence orbital was expanded into four gaussians. The α parameter in Eq. (8) was obtained by fitting the atomic ground-state orbital energies as has been described previously,[1,10,11] and for iodine has the value 3.1814 a.u.$^{-1}$ The properties chosen for comparison are the orbital energies of the five occupied valence orbitals, the equilibrium bond length and the vibrational frequency. The effective-potential calculations in each case required less computer time than the corresponding full SCF calculation by a factor of 150.

The second and third columns of Table I show the effect of using a pseudopotential of the form given by Eq. (3), setting ε_v to be the lowest molecular valence-orbital energy $\varepsilon_v^{(1)}$, compared to Eq. (6) in which all the ε_v^i are found iteratively. The most apparent difference is seen to be an improvement in the accuracy of the orbital energies relative to the full SCF results.

In computing the local potential functions, it is clear from Eqs. (19), (20) and (21) that there will be a different W^i for each symmetry of valence basis function. For example, in the minimal basis of the iodine atom there will be one for χ_v^s and a different one for χ_v^p. These hopefully should be smoothly decreasing in the valence region, and W^s should be nearly equal to W^p. This is indeed seen to be the case from Table II, which shows, in the first four columns of data, the core and valence potentials W_c and W_v appropriate to the χ_v^s and χ_v^p atomic pseudowavefunctions.

Although W^s and W^p could be used separately in a molecular valence-electron calculation, we will use here a single function, $\bar{W}$, to represent both in order to draw a valid comparison with the use of the exponential approximation, W^{exp}. Thus we will simply define $\bar{W}$ as the least-squares fit to $W^i(\chi_v^i)^2$ for all atomic symmetries, i, at each point in space, so that for the iodine atom

$$\bar{W} = \frac{W^s(\chi_v^s)^4 + W^p(\chi_v^p)^4}{(\chi_v^s)^4 + (\chi_v^p)^4} . \tag{22}$$

This function is shown in the fifth column of Table II, and W^{exp} is presented for comparison in the sixth column.

In performing molecular computations in a contracted gaussian basis set, it is clearly desirable to have the local potential expressed as an expansion in gaussian functions,

$$\bar{W}(r) = N[1 - \Sigma c_i \exp(-e_i r^2)]/r. \tag{23}$$

This expansion was found to converge, after inclusion of five or more terms, to approximately three significant figures of the properties given in Table I. The weighting factor employed was the denomimator in Eq. (22) multiplied by r^2. The coefficients and exponents of this expansion are shown in Table III.

The properties found using this potential with the pseudopotential defined by Eq. (6) (using the molecular pseudowavefunctions) are shown in the fourth column of Table I. The differences from the results obtained with W^{exp} are again seen to be relatively small.

V. Discussion

The advantages of employing the Phillips-Kleinman expression in molecular calculations were stated in Section I. Further, its use leads to Eqs. (5) and (10). These equations in turn allow construction of the simple and general functions of the form (19), (20) and (21). These local potential functions have the properties that (1) the functional form of W^i is not constrained to to any analytical approximation, and (2) the atomic ϕ_v^i and χ_v^i functions need not be solutions of an atomic secular equation, thereby permiting the use of, for example, molecularly-optimized basis sets.

The purpose of the present paper has been to describe the origin of some of the terms appearing in the molecular effective potential. Although the results reported here are somewhat more precise than we had previously thought possible for this row of the Periodic Table, it seems very likely that more precise valence-electron calculations are possible. Parameterization schemes[4,12] have been found to work well for compounds of light elements, but become extremely complex for the heavier elements since they must implicitly simulate Eq. (3). However the accuracy of the valence-electron approximation itself is not yet well established for compounds such as I_2. Other pseudopotential results for I_2 are not yet readily available, although

Kahn et al.[13] report an equilibrium bond length of 2.81 Å using a somewhat more complex basis set in an MCSCF formalism. The experimental value is 2.667 Å.[14] Recently Barthelat, Durand and Serafini,[15] using a double-zeta basis set, have obtained orbital energies for I_2 differing from the corresponding full SCF results by an average of 12.5%, and an equilibrium bond length and vibrational frequency differing by 8% and 17.4% respectively.

An apparent minor improvment that might be made in the computational approach described here would be the use of a different W^i function for each atomic symmetry type. The problems that arise in this type of calculation, due to the fact that a basis function on nucleus A need not have a simple atomic symmetry in the region of nucleus B, have been treated approximately by several authors.[5,8,12] However, since the W^s function is very similar to the W^p function, it seems likely that their use in molecular calculations would be quite insensitive to the exact fashion in which this angular-momentum dependence were treated.

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Table I. Comparison of the orbital energies, equilibrium bond lengths and vibrational frequencies of I_2 obtained by three effective-potential formulations and by a full-SCF calculation.

pseudopotential	Eq.(3), $\epsilon_v = \epsilon_v^{(1)}$	Eq.(6)	Eq.(6)	SCF
model potential	Eq.(8)	Eq.(8)	Eqs. (19)-(21)	
valence orbital energies (au)				
$\varepsilon_{1\,9\sigma}$	-0.8019	-0.8117	-0.8143	-0.8063
$\varepsilon_{2\,0\sigma}$	-0.6824	-0.6787	-0.6792	-0.6747
$\varepsilon_{2\,1\sigma}$	-0.3962	-0.3721	-0.3718	-0.3769
$\varepsilon_{1\,1\pi}$	-0.3824	-0.3592	-0.3585	-0.3571
$\varepsilon_{1\,2\pi}$	-0.3196	-0.2903	-0.2886	-0.2878
bond length (Å)	2.708	2.605	2.575	2.737
vibrational frequency (cm^{-1})	230.0	247.0	262.6	263.6

Table II. The core and valence contributions to the atomic local potential of Iodine, its total average value, $\bar{W}$, and the exponential approximation, W^{exp}, as a function of the distance r from the nucleus. All values are in atomic units. The maximum in the χ_v^s function is at approximately 1.5 au and for the χ_v^p function at 1.6 au.

r	W_c^s	W_c^p	W_v^s	W_v^p	$\bar{W}$	W^{exp}
0.5	67.76	66.13	3.56	3.63	71.20	73.25
1.0	43.41	43.32	0.54	0.49	43.92	44.09
1.5	30.43	30.44	0.04	0.02	30.47	30.41
2.0	22.97	22.97	0.0	0.0	22.96	22.96
2.5	18.38	18.39	0.0	0.0	18.39	18.39
3.0	15.32	15.33	0.0	0.0	15.33	15.33

Table III. Coefficients and exponents of the gaussian expansion of the local potential $\bar{W}$. The form of the expansion is defined by Eq.(23).

c_i	e_i
-0.60515	5.1547
0.71330	4.5158
0.24807	2.0895
0.02046	0.8308
0.00137	0.1255